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**Patentanmeldung Nr. Patent application No. Demande de brevet n°**

03016889.2

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SUISSE

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Si aucun titre n'est indiqué se referer à la description.)

Method for granting a chemical compound to a support substrate

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)  
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**Method for grafting a chemical compound to a support  
5 substrate**

The invention relates to a method for grafting a chemical compound to a predetermined region of a support substrate.

10

Rapid and simple methods for creating micro- and nano-structured surfaces or three-dimensional structures, such as tubes or channels, in the support substrate are desirable. These micro- and nano-structured surfaces or  
15 three-dimensional structures have designed features, structures or aspects with lateral or vertical dimensions on the order of from one nanometer to several microns. To allow these structures a broad field of applications, it is desired that these micro- and nano-structured surfaces  
20 can be made having a wide variety of chemical functionalities and physical properties. Properties of interest include reactivity or binding characteristics towards particular chemical species or hydrophobic or hydrophilic properties. It is further desirable to be  
25 able to create these structures having these functionalities or properties structured in the form of nano- or micro-scale arrays or other geometric structures. For example, such micro- and nano-structured materials can find application in combinatorial  
30 chemistry, (bio)-sensing, membrane technologies, liquid repellents, adhesives, lubricants, anti-fogging coatings, and micro- and nano-electronic and magnetic devices. Alternatively, they can be used to create biologically compatible surfaces or to offer medical or bio-  
35 technological active surfaces.

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One form of such suitable materials are known as "polymer brushes", and they are described, for example, by Freemantle in Chemical & Engineering News, April 14, 2003, p. 41-45. In these materials polymer chains are

5 tethered at one end, usually by covalent bonding, to a surface or an interface. Such polymer brushes can be made by the "grafting-to" or "grafting-from" methods. The grafting-to method involves the reaction of preformed

10 polymer chains with a surface to anchor the chains on the surface. The grafting-to method has the disadvantage of giving surfaces with only low grafting densities (number of polymer chains/unit area). In particular, polymer chains at the interface of a solution and substrate are

15 in the form of brushes only if the grafting density is high enough to force the chains to adopt elongated rather than coiled conformations.

In the grafting-from method, initiator molecules are immobilized on a surface and exposed to a monomer under

20 appropriate polymerization conditions. The grafting-from method currently suffers from the disadvantages of requiring multiple steps for creating, activating, and reacting initiator sites, and they are typically created only on comparably expensive special gold or silicon

25 surfaces. An example of such a reaction scheme is disclosed from U. Schmelmer and co-workers in Angew. Chem. Int. Ed. 42, No. 5 (2003) 559-563, especially in Figure 1 of this disclosure.

30 In view of the several afore mentioned drawbacks of the actually known methods, it would be a desired aim of the invention to have simple means for creating polymer brushes on surfaces.

~~It is an object of the present invention to provide a method for creating polymer brushes on surfaces which is simple and efficient.~~

~~The method according to the invention is characterized in that the initiator molecules are immobilized on the surface and the monomer is added to the surface.~~

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This aim is achieved according to the present invention by a method for grafting a chemical compound to a predetermined region of a support substrate, comprising:

- 5 a) irradiating selectively the support substrate with electromagnetic radiation and/or particle radiation in order to both define said predetermined region and to form at least one reactive functional group or a precursor thereof in said predetermined region
- 10 of the support substrate;
- b) exposing the irradiated support substrate to said chemical compound or to a precursor thereof.

Therefore, only these very few steps are needed to

15 effectively grafting the desired chemical element or compound, such as an organic compound, to the predetermined regions of the support substrate. Moreover, the irradiation step can be carried out in a vastly flexible manner and allows to generate numerous distinct

20 shapes of the predetermined regions. Further, micro- or nano-scale regions in the support substrate capable of forming reactive functional groups or precursor thereof upon exposure to particle or electromagnetic irradiation can be easily achieved. Thereby, in view of the above

25 mentioned invention, a reactive functional group is considered as being any modified structural unit generated by the irradiating step that is able to act as a reactive site for the chemical compound to be grafted thereupon.

30

The step of exposing can be a simultaneous or subsequent step, when the irradiated support substrate is exposed preferably to one or more radically polymerizable monomer species. The physical properties, height, penetration

35 depth and spatial resolution of the micro- or nano-scale modification of the support substrate can be conveniently varied by controlling the various parameters in the

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irradiation or exposing steps. There is no specific limitation as to the substrate depth that is modified. The modification can be primarily just on the surface or extend through the entire thickness of the substrate.

- 5 Examples of these parameters in the irradiation process include the type and energy of the radiation, the total dose, the dose rate and the irradiation atmosphere.

- 10 With respect to the type of the support substrate used in this invention there does not exist any specific limitations. Any organic or inorganic substrate capable of forming reactive functional groups upon exposure to ionizing irradiation are suitable. The composition and chemical structure of the substrate is also not limited.

- 15 The substrate will generally be selected according to the desired properties for the substrate, for example, mechanical properties, or according to the desired properties for the non-structured regions such as hydrophilic or hydrophobic or reactive or inert. Some  
20 non-limiting examples of substrates include polymers such as fluoropolymers like PTFE, FEP, PVDF or ETFE or polyolefins like polyethylene or polypropylene. Additionally, even the form of the substrate is not specifically limited and includes coatings, films, and  
25 shaped particles.

- 30 With respect to the reactive functional group dealing as the receptor nuclei for the latter grafting a non-limiting number of examples for the reactive functional groups introduced by the irradiation can be mentioned. These examples include hydroperoxides, peroxides or such

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particle radiation such as electron beam. In particular, the irradiation energy and type can be varied to control the depth of functionalization of the latter micro- or nano-grafting into the support substrate. For example,

5 the wavelength of the electromagnetic radiation or accelerating potential for the electron beam will have a strong influence on the penetration depth as it can be derived from physical penetration theory. The wavelength also determines the minimum spatial resolution in

10 patterning. The total dose and dose rate influence the total number and thus density of reactive sites (reactive functional groups) formed.

Furthermore, the irradiation atmosphere can be controlled

15 to yield oxygen-containing or other element-containing reactive sites in the substrate. In some cases a vacuum or inert irradiation atmosphere might be selected in order to minimize degradation of the support substrate. In the case of polymeric substrates, the irradiation

20 conditions can be selected in order to preferentially bring about crosslinking or chain scission or even ablation of the polymer substrate.

However, masks or stencils and interference or projection

25 lithography or other methods known in the prior art can be used to create the micro- or nano-scale pattern of reactive sites on and/or in the support substrate.

The method used to micro- or nano-graft the substrate is

30 not specifically limited. For example, the grafting can be carried out simultaneously along with the irradiation process, or the grafting can be done in a post-irradiation step. If the grafting is done in a subsequent step, the irradiated substrate may be stored at room

35 temperature or at reduced or at elevated temperature and/or under inert atmosphere if the reactive sites are unstable.

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Parameters in the grafting process can be varied in order to optimize the resolution of the grafting process. For example, the sharpness and height of the grafted micro-  
5 or nano-regions can be enhanced or controlled by proper selection of the monomer concentration or grafting temperature. Other parameters such as the choice of solvent or the use of chain-transfer or terminating agents or living polymerization agents or methods can  
10 also be used to influence these properties.

The physical form of the monomer is also not specifically limited in this invention. For example, the monomer may be applied to the substrate in the form of a gas or a  
15 liquid, and the monomer may be either pure or diluted with a solvent or inert material and/or as a mixture with one or more additional monomers. Any radically active monomer may be used in this invention including vinyl, styrenic or acrylic monomers. Monomers can be selected in  
20 this invention according to the properties that are desired for the micro- or nano-structured grafted regions. For example, if it is desired that the grafted region be hydrophilic in nature, monomers having polar or hydrogen bonding functional groups such as amine, amide,  
25 thiol, hydroxy, carboxyl, carboxylic acid, or ester may be selected. Further non-limiting examples of hydrophilic monomers include acrylic acid and its salts, methacrylic acid and its salts, methyl methacrylate, sulfonated styrene and its salts, styrene sulfonic acid and its  
30 salts, or vinyl sulfonic acid. If the grafted regions should be hydrophobic, fluorinated or hydrocarbon

~~monomers can be used. Non-limiting examples include~~

~~acrylic acid, methacrylic acid, methyl methacrylate, styrene, styrene sulfonic acid, vinyl sulfonic acid, and hydrocarbon monomers.~~



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The modified grafted regions in the support substrates are characterized in that they are micro- or nano-scale regions, either substantially 2-dimensional or 3-dimensional, that contain the grafted polymer chains.

5 There is no specific limitation on the shape or form of these grafted regions, and for example, they may be lines, dots, grids, mesh, stenciled, channels, tubes, cylinders or any other suitable arbitrary geometric shapes. These grafted regions may be either nano- or  
10 micrometer scale in height. With reference to the aforementioned 3-dimensional shape, the grafted regions may also penetrate into the interior of the modified material and/or may be detached from the surface in a subsequent step.

15 Without any limitation to any application a person skilled in the art may have apparently understood from the description, the application of these micro- or nano-grafted materials is proposed for use in the fields of  
20 combinatorial chemistry, membrane technology, surface science (including repellents, adhesives and lubricants and anti-fogging and other coatings), sensing, information storage, chromatography, separation processes, electrochemical synthesis, medical and bio-  
25 technical material handling, electrochemical energy storage and conversion devices, and electronic and magnetic devices. A person skilled in the art will be able to select substrates, chemical elements or compounds, and predetermined regions appropriate for any  
30 of these applications. A non-limiting example is a micro- or nano-grafted material modified through its thickness with functional groups useful for the conduction of ions or other species. Non-limiting examples of such functional groups include acids, bases, or amphoteric  
35 groups.

The various features and advantages of this invention will become apparent to those skilled in the art from the following detailed description of the currently preferred embodiment. The drawings that accompany the detailed  
5 description can be briefly described as follows:

Figure 1 is a 100  $\mu\text{m}$  ETFE-film as received;

10 Figure 2 is a 100  $\mu\text{m}$  ETFE-film, flattened at 230°C;

Figure 3 is a 100  $\mu\text{m}$  ETFE-film, flattened at 230°C, electron beam exposed (line 1a) and grafted with 10% acrylic acid for 20 min;

15 Figure 4 is a 100  $\mu\text{m}$  ETFE film, flattened at 230°C, X-ray exposed (exposure 1, box 1) and grafted with 5% acrylic acid; and

20 Figure 5 is a 100  $\mu\text{m}$  ETFE-film, flattened at 230°C, X-ray exposed (interference set-up, period: 100 nm) and grafted with 5% acrylic acid for 15 min at 50°C.

25 For the examples, Nowoflon ET-6235 films having thicknesses of 25, 50, and 100  $\mu\text{m}$  and extruded roll widths of 155 cm designated here as N-25, N-50, N-100 were purchased from Nowofol GmbH, Siegsdorf, Germany. The average molar weight of the Dyneon ET 6235 copolymer used  
30 to make these films is approximately 400,000 Dalton.

To obtain a flat test surface, a piece of ETFE film 2 (Nowoflon ET-6235, 100  $\mu\text{m}$ , "N-100") was placed between two polished 8" silicon wafers, or 1.5 x 1.5 cm<sup>2</sup> pieces  
35 of silicon. The test setup which is optional is shown in Figure 1. The test setup which is optional is shown in Figure 1.

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results in a reduction of film thickness of about 5-10%, and a drastic reduction in surface roughness as it can be seen from the comparison of the initial ETFE film 2 and the flattened ETFE film 4 in the figures 1 and 2.

5

Electron beam exposures were done with a LION-LV1 e-beam system (Leica Microsystems, Jena, Germany). The beam energy was 2.5 keV. The "continuous path control" mode was used to obtain lines with the desired doses in our exposures. The beam defocus was adjusted to control the exposed linewidth.

10

X-ray exposures were done at the "X-ray Interference Lithography" beamline of the Swiss Light Source. The beamline uses undulator light with a central wavelength of 13.5nm (92 eV) and approximately 2% spectral bandwidth. The incident x-ray power on the sample was several mW/cm<sup>2</sup> and the delivered dose was controlled with a fast beam shutter. A shadow mask in proximity to the sample to define the exposed areas on the sample. A TEM-grid with features in the range of  $\geq 50 \mu\text{m}$  was used as a shadow mask in proximity to the sample to define the exposed areas in the sample. X-ray interference exposures were done as described by Harun Solak et al.,

15

20

25

Pieces of micro- or nano-scale irradiated ETFE films were placed in small glass tube reactor equipped with purge gas inlets and outlets that can be sealed by means of stopcocks. The reactor is then filled with an aqueous solution of acrylic acid monomer and then closed. After purging the reactor for 1 hr with nitrogen, the reactor is sealed by first closing the outlet, and then the inlet. The reactor was then placed in a water bath preheated to the desired reaction temperature. When the reaction time is over, the reactor seal is broken and the sample is gently taken out of reactor. The sample was

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then rinsed four times with deionised water and then dried at room temperature.

The following reaction conditions were used:

5

	Acrylic Acid conc./%	Temperature/°C	Reaction Time/min
1.	10	60	20
2.	5	60	20
3.	5	50	15

10 The grafted samples were inspected in an optical microscope and characterized using atomic force microscopy (AFM). A Digital Instrument Nanoscope III (Dimension 3100) was used in the tapping mode using Nanosensor NCH type AFM tips with a resonance frequency of 330 kHz.

15 First measurements on e-beam exposed and grafted samples were conducted at the PSI as well as first characterization of X-ray exposed (shadow mask and interference set-up) and grafted samples.

20 Figure 3 shows a typical AFM image of a line structure 6 produced by e-beam irradiation and grafting. The line width is depending on the defocus of the e-beam (which is not yet optimized for the used material) and on the dose supplied. Using the 10% acrylic acid solution to graft a sample exposed to low dose, a structure with a very sharp definition of the borders and a height in the range of

25

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Flattened ETFE 4 was exposed to various doses of x-rays through a TEM grid used as a shadow mask. After grafting with 5% acrylic acid, the structures ( $\geq 50 \mu\text{m}$ ) were clearly visible in the optical microscope. The height of the grafted structures as measured with the AFM (Figure 4) was in the range of 300 nm with very little dependence on the used dose of x-rays.

- 10 The AFM image (Fig. 5) of a sample which was irradiated in the x-ray interference set-up and grafted with 5% acrylic acid shows a pattern with a period of 100 nm.

The foregoing description is exemplary and not just a material specification. The invention has been described in an illustrative manner, and should be understood that the terminology used is intended to be in the nature of words of description rather than of limitation. Many modifications and variations of the present invention are possible in light of the above teachings. The preferred embodiment of this invention have been disclosed, however, one of ordinary skill in the art would recognize that certain modifications are within the scope of the invention. It is understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described. For that reason, the following claims should be studied to determine the true scope and content of this invention.

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Claims

5

1. Method for grafting a chemical compound to a predetermined region of a support substrate (4), comprising:

10

a) irradiating selectively the support substrate (4) with electromagnetic radiation and/or particle radiation in order to both define said predetermined region and to form a reactive functional group or a precursor thereof in said predetermined region of the support substrate;

15

b) exposing the irradiated support substrate to said chemical compound or to a precursor thereof.

2. Method according to claim 1, characterized in that

20

the step of exposing is carried out simultaneously during the step of irradiating.

3. Method according to claim 1, characterized in that

25

the step of exposing is carried out successively after the step of irradiating.

4. Method according to any of the preceding claims, characterized in that

30

the properties of the predetermined region are controlled in dependency of the parameters of the irradiating step.

5. Method according to claim 4, characterized in that

35

the properties of the predetermined region are controlled in dependency of the parameters of the irradiating step.

chemical properties, height, penetration depth and spatial resolution.

- 5 6. Method according to claim 4 or 5,  
characterized in that  
as parameter of the irradiating step are considered at  
least one of the group comprising type of radiation,  
energy of radiation, total dose of radiation and  
irradiation atmosphere.
- 10 7. Method according to any of the preceding claims,  
characterized in that  
the support substrate (2) is chosen in the dependency of  
at least one property of the group containing desired  
15 reactive functional group or a precursor thereof, desired  
property of the support substrate and desired property of  
the non-irradiated regions.
- 20 8. Method according to claim 7,  
characterized in that  
the support substrate is of organic or inorganic type  
and/or of reactive or inert type and/or hydrophilic or  
hydrophobic type.
- 25 9. Method according to any of the preceding claims,  
characterized in that  
the reactive functional group is at least one selected  
from the group comprising hydroperoxides, peroxides, or  
any type of radicals such as alkyl radical, oxy radical  
30 and peroxy radical.
10. Method according to any of the preceding claims,  
characterized in that  
UV or X-ray radiation is used as electromagnetic  
35 radiation.
11. Method according to claim 10,

characterized in that  
interference lithography is used to generate the  
predefined regions of reactive functional groups.

5

12. Method according to any of the preceding claims,  
characterized in that  
electron beam is used as particle radiation.

10

13. Method according to any of the preceding claims,  
characterized in that  
the compound or the predecessor of the compound is an  
organic monomer that is applied in form of a gas  
comprising the monomer or a liquid comprising the monomer  
to the predetermined region.

15

14. Method according to claim 13,  
characterized in that  
the monomer is a radically active monomer.

20

15. Method according to claim 13 or 14,  
characterized in that  
the monomer is used as a pure liquid or is diluted with a  
solvent or an inert material and/or a mixture with one or  
more additional monomers.

25

16. Method according to any of the preceding claims,  
characterized in that  
the predetermined regions formed in the shape of a three  
dimensional tube or channel.

30

17. Method according to any of the preceding claims,  
characterized in that

the grafted material is detached from the support

structure or the support structure is dissolved

to obtain the grafted material



18. A micro- or nanostructured material prepared by the process of any of the claims 1 to 17.

5 19. A micro- or nanostructured material of claim 18, characterized in that the substrate is a polymer and the compound is a polymer.

10 20. A micro- or nanostructured material of claim 18 or 19, characterized in that the non-structured regions are hydrophobic and the modified grafted regions are hydrophilic.

15 21. A micro- or nanostructured material of claim 18 or 19, characterized in that the non-structured regions are hydrophilic and the modified grafted regions are hydrophobic.

20 22. A micro- or nanostructured material of any of the preceding claims 18 to 21, characterized in that the modified grafted regions comprises polymer brushes.

25 23. A micro- or nanostructured material of any of the preceding claims 18 to 22. characterized in that the compound is selected from the group comprising acrylic, vinyl and styrenic polymers.

30 24. A micro- or nanostructured material according to any of the preceding claims 18 to 23 characterized in that the compound is selected from the group comprising  
35 polyacrylic acid and its salts, polymethacrylic acid and its salts, polymethylmethacrylate, polystyrene,

sulfonated polystyrene and its salts, polyethylene, polytetrafluoroethylene, and polypropylene.

25. A micro- or nanostructured material according to any  
5 of the claims 18 to 24,  
characterized in that  
the compound has functional groups capable of selectively  
binding with chemical elements, functional groups or  
molecules present in a gaseous or liquid phase.

10 26. A micro- or nanostructured material according to any  
of the preceding claims 18 to 25,  
characterized in that  
the compound has functional groups selected from the  
15 group comprising amine, amide, thiol, hydroxy, carboxyl,  
carboxylic acid, or ester functional groups.

27. A micro- or nanostructured material to any of the  
preceding claims 18 to 26,  
20 characterized in that  
the substrate is modified through its entire thickness.

28. A micro- or nanostructured material of any of the  
preceding claims 18 to 27,  
25 characterized in that  
a membrane is used for a separation, transport or  
conduction application.

29. A micro- or nanostructured material of claim 28,  
30 characterized in that  
the membrane is used in an electrochemical cell.

30. A micro- or nanostructured material of any of the  
preceding claims 18 to 29,  
35 ~~characterized in that~~

31. A micro- or nanostructured material of claim 30, characterized in that the polymer film is selected from the group comprising PTFE, FEP, ETFE, PVDF, PE, and PP.

5

32. The use of the micro- or nanostructured material of any of the preceding claims 18 to 31 in a combinatorial chemistry, biotechnological, or separation application.

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**Abstract**

5

According to the present invention a method for grafting a chemical compound to a predetermined region of a support substrate (4) is disclosed, comprising:

10

a) irradiating selectively the support substrate with electromagnetic radiation and/or particle radiation in order to both define said predetermined region and to form at least one reactive functional group or a precursor thereof in said predetermined region of the support substrate;

15

b) exposing the irradiated support substrate to said chemical compound or to a precursor thereof.

20

Therefore, only these very few steps are needed to effectively grafting the desired chemical compound, such as an organic compound, to the predetermined regions of the support substrate. Moreover, the irradiation step can be carried out in a vastly flexible manner and allows to generate numerous distinct shapes of the predetermined regions. Further, micro- or nano-scale regions in the

25

support substrate capable of forming reactive functional groups or precursors thereof upon exposure to particle or electromagnetic irradiation can be easily achieved.

Fig. 5

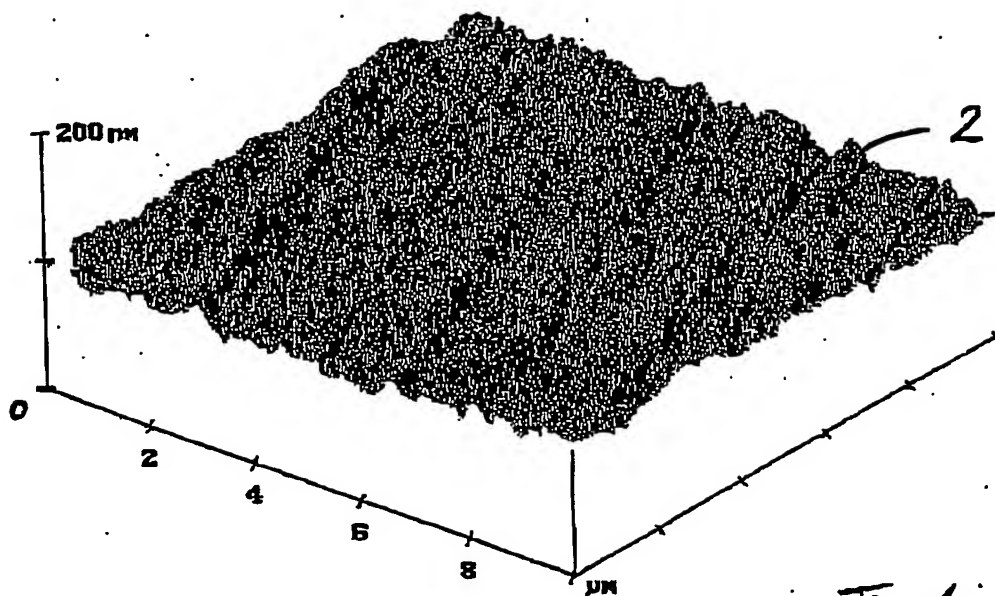


Fig. 1

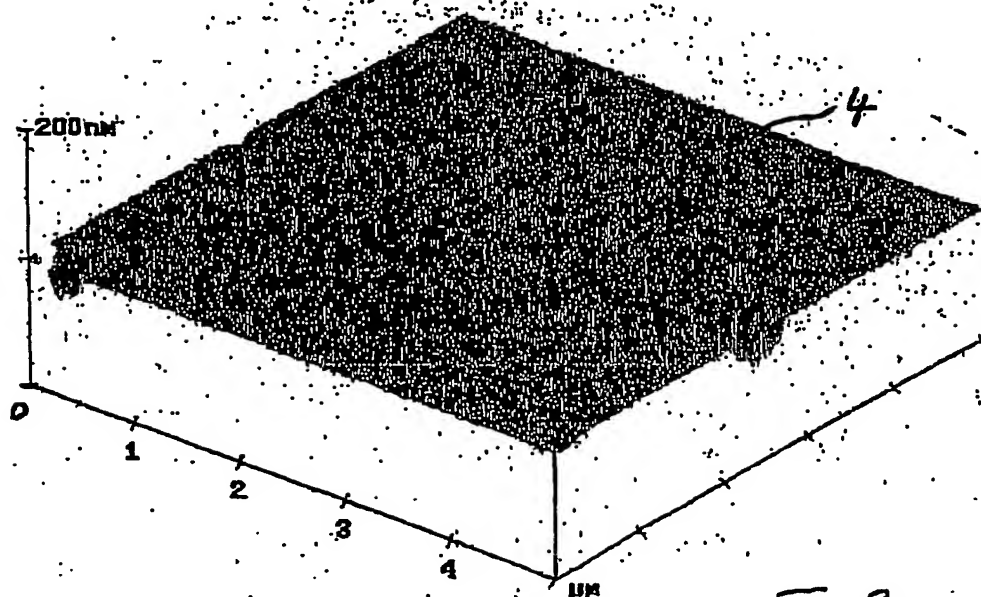


Fig. 2

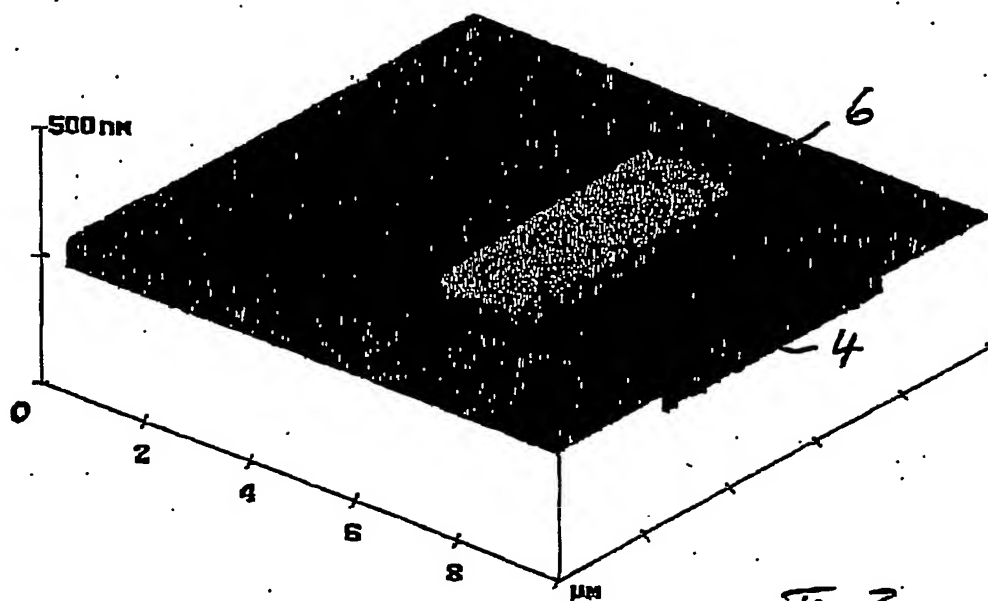
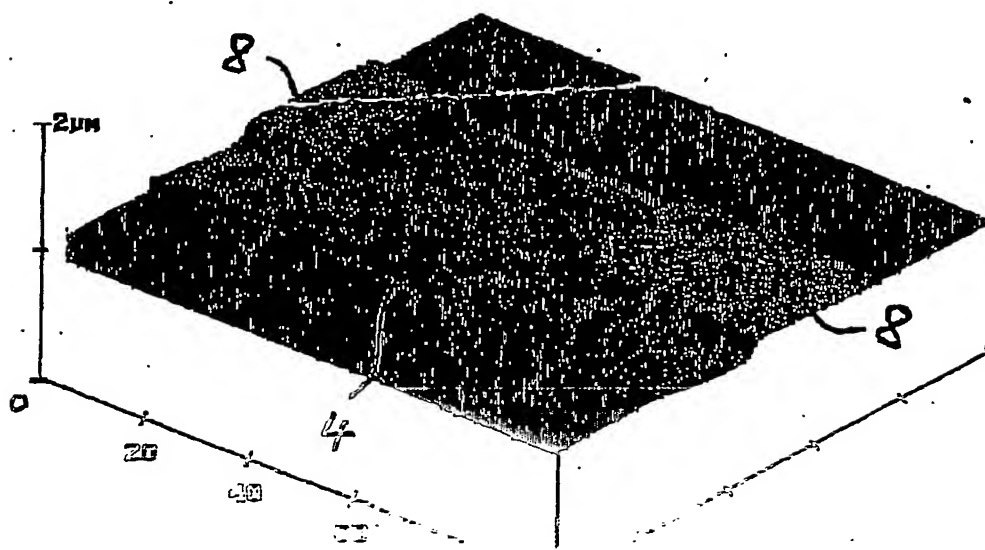


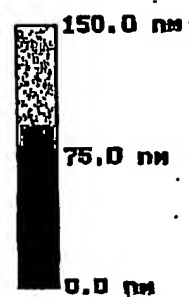
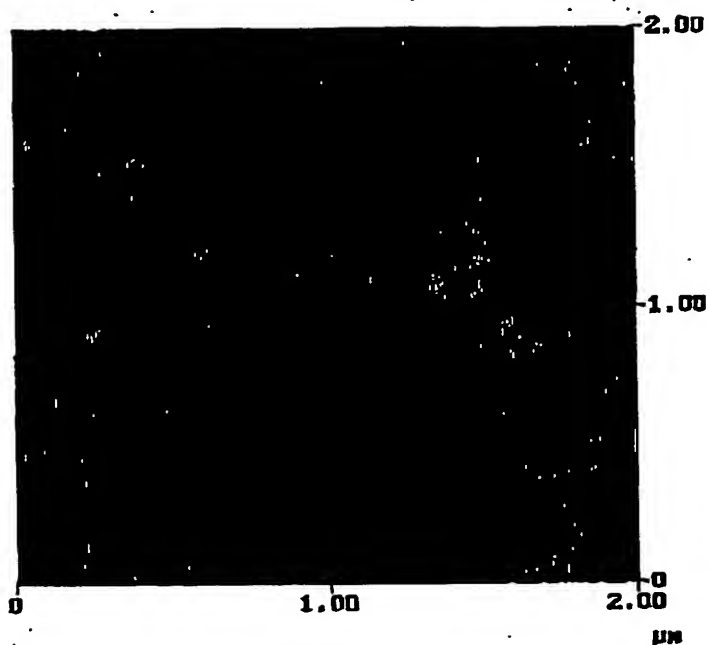
Fig. 3



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Digital Instruments NanoScope  
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Scan rate 0.5003 Hz  
Number of samples 512  
Image Data Height  
Data scale 150.0 nm

Fig. 5

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